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CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER:
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U.S. APPL. NO. (If known, see 37 CFR 1.5)

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INTERNATIONAL APPLICATION NO.:
PCT/SE99/01046

INTERNATIONAL FILING DATE:
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PRIORITY DATE CLAIMED:
12 June 1998 (12.06.98)

TITLE OF INVENTION: FUEL CELL

APPLICANT(S) FOR DO/EO/US: Bin ZHU

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
 2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
 3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
 4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
 5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ has been transmitted by the International Bureau. (see attached copy of PCT/IB/308)
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
 6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
 7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
 8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
 9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
 10. ☐ A translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Item 11. to 16. below concern document(s) or information included:
11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
 12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
 13. ☒ A **FIRST** preliminary amendment.
 14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
 15. ☐ A substitute specification.
 16. ☐ A change of power of attorney and/or address letter
 16. ☒ Other items or information: International Preliminary Examination Report (PCT/IPEA/409), International Search Report (PCT/ISA/210), Application Data Sheet

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CALCULATIONS PTO USE ONLY

17. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):**

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$ 1,000.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$ 860.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$ 710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$ 690.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$ 100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

\$ 1000.00

Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492(e)).

\$

CLAIMS**NUMBER FILED****NUMBER EXTRA****RATE**

\$

Total claims 5 - 20 = 0 X \$18.00 \$

Independent claims 1 - 3 = 0 X \$80.00 \$

MULTIPLE DEPENDENT CLAIMS(S) (if applicable) + \$260.00 \$

TOTAL OF ABOVE CALCULATIONS =

\$ 1000.00

Reduction of 1/2 for filing by small entity, if applicable. Applicant claims Small Entity Status under 37 CFR 1.27. +

\$

500.00

SUBTOTAL =

\$

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Processing fee of \$130 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.49(f)).

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a. ☒ A check in the amount of \$ 500 to cover the above fees is enclosed.b. ☐ Please charge my Deposit Account No. **25-0120** in the amount of \$ to cover the above fees. A duplicate copy of this sheet is enclosed.c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required by 37 CFR 1.16 and 1.17, or credit any overpayment to Deposit Account No. **25-0120**. A duplicate copy of this sheet is enclosed.

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December 11, 2000

By



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PATENTS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Bin ZHU

Serial No. (unknown)

Filed herewith

FUEL CELL

PRELIMINARY AMENDMENT

Commissioner for Patents

Washington, D.C. 20231

Sir:

Prior to the first Official Action and calculation of the filing fee, please substitute Claims 1-8 as originally filed, which appear on pages 14-15, with Claims 1-4 as filed in the Article 34 amendment of October 10, 2000. The page containing Claims 1-4 is marked "AMENDED SHEET" and is attached hereto. Following the insertion of Claims 1-4, please amend these claims as follows:

IN THE CLAIMS:

Claim 3, line 1, cancel "or 2".

PLEASE ADD CLAIM 5:

--5. A fuel cell according to claim 2, wherein the electrodes comprises binary oxides, such as $A_xB_yO_z$ (A, B=Li, Mg, Ca, Sr, Cr, Fe, Co, Ni, Mn, Cu, Y, La, Ce, Zr, Ti, etc.), typically, Li_xMo_y (M=Ni, Co, Mn), $Ce_{1-x}B_xO_{2-y}$, MnO_2 and $La_{1-x}Sr_xMn(Co)O_3$.--

Bin ZHU

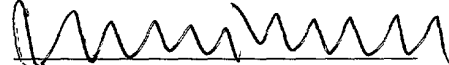
R E M A R K S

The above changes in the claims merely place this national phase application in the same condition as it was during Chapter II of the international phase, with the multiple dependencies being removed. Following entry of this amendment by substitution of the pages, only claims 1-5 remain pending in this application.

Respectfully submitted,

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528 Rec'd PCT/PTO 11 DEC 2000

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3/PARTS

A fuel cellField of the invention

5 This invention relates to a fuel cell and more particularly the invention relates to an intermediate temperature fuel cell.

The present invention is also relevant to catalysts and membrane reactors, such as hydrogen generator and penetration devices.

10 Furthermore, the invention is also relevant to devices for treatment of hazardous gases, such as desulphurisation, and waste chlorine treatment etc.

Background of the invention

15 A fuel cell is an electrochemical cell which can continuously convert chemical energy of a fuel and an oxidant to electrical energy by a process involving an essentially invariant electrode-electrolyte system. Fuel cells work at high efficiency with emission levels far below the most strict standards. Fuel cell systems have the advantage of being modular, therefore they can be built in a wide range of power requirements, from a few hundred watts up to megawatts.

20 The basic principles of a fuel cell are those of well known electrochemical batteries. The difference is that in the case of batteries, the chemical energy is stored in substances located inside them. When this energy is converted to electrical energy, the battery must be thrown away (primary batteries) or recharged (secondary batteries).
25 In a fuel cell, the chemical energy is provided by a fuel and an oxidant stored outside the cell in which the chemical reactions take place.

30 The fuel cell comprises an anode, an electrolyte and a cathode. The fuel is oxidised at the anode, and the oxidant is reduced at the cathode. The reactions can be described as "cold combustion", giving water as combustion product. In between the anode/cathode is the electrolyte.

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During the cold combustion in the fuel cell electrical work is produced corresponding to a change in free energy determined by the equation of Gibbs-Helmholtz (1) as follows:

5
$$\Delta G = \Delta H - T \Delta S = U \cdot n \cdot F \quad (1)$$

ΔH being the change in enthalpy in J/mole when water is formed from its elements (corresponding to the amount of heat liberated at open combustion of hydrogen gas at constant pressure and temperature), T is the absolute temperature in K and ΔS the change in entropy in J/K*mole; U is the open voltage of the fuel cell, n is the number of electrons consumed at the reaction ($n = 4$ for each water molecule formed for a hydrogen/oxygen cell) and F is Faraday's constant (96 485 As/mole).

15 The current density for fuel cell electrodes is limited by the reactants and normally reaches less than A/cm².

For practical reasons, fuel cell systems are simply distinguished by the type of electrolyte used and the following names and abbreviations are now frequently used in literature: alkaline fuel cells (AFC), phosphoric acid fuel cells (PAFC), solid/molten state cells (SSFC) such as: molten carbonate fuel cells (MCFC), solid oxide fuel cells (SOFC) and proton exchange membrane fuel cells (PEMFC). The fuel cells mentioned above will be described in more detail below.

25 The alkaline fuel cell (AFC) is used for instance in the space and military industry, for instance in submarines.

Solid/molten state cells (SSFC) of today are of three basic types, PEMFC (Polymer electrolyte), MCFC (Molten Carbon) and SOFC (Solid Oxide).

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Efforts have been made to construct solid state fuel cells using carbonate melts (MCFCs), but they usually have low efficiency.

PEMFCs use proton-exchange polymer membranes as electrolytes. The presence of water in the membranes limits the operational temperatures to below 100 °C. This causes slow electrode kinetics and low tolerance of electrodes to fuel impurities such as carbon monoxide (CO). As a result, neither hydrocarbons, nor hydrogen from hydrocarbon reforming (inevitably with CO) can be used as fuels for the PEMFCs. A further development thereof is polymer membranes, which can resist higher temperatures, such as 200 °C.

MCFCs use molten alkali carbonates retained in a matrix as the electrolyte. Such a device requires an operation temperature of about 650 °C to maintain a molten state with sufficient ionic conductivity. Although some MCFCs have been on the market, there are still several technological issues critically hindering the commercialisation progress, mainly concerning serious material corrosion problems.

SOFCS usually use ceramic membranes (YSZ). Limited by its ionic conductivity, the YSZs require an operational temperature of about 1000 °C, thereby resulting in considerable constraints on the materials used for interconnection, sealing and construction. However, as the electrolyte is solid-a mixture of yttria (Y₂O₃) and zirconia (ZrO₂)-problems with liquid handling and corrosion are avoided. Charge transfer in the electrolyte is done by oxygen ions (O²⁻). Anodes made of nickel/zirconium oxide cermet were shown to be suitable; cathodes of lanthanum manganate (LaMnO₃) have been used, but require still some additional research.

Electrode reactions are summarised for the proton conducting case as follows:

Anode reaction: $\text{H}_2 (\text{g}) \rightarrow 2\text{H}^+ + 2\text{e}^-$

Cathode reaction: $2\text{H}^+ + 2\text{e}^- + \frac{1}{2} \text{O}_2 (\text{g}) \rightarrow \text{H}_2\text{O} (\text{g/l})$

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Overall reaction: $\text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow \text{H}_2\text{O} (\text{g})$

As the cathodic reaction uses oxygen only (or air) as oxidant, recirculation of carbon dioxide from the anode exhaust is not necessary, and thereby simplifies the system considerably. Carbon monoxide does not poison the electrodes and can also be used as a fuel. Difficulties in the development of SOFCs arise from the instability of the intercell connections, i. e. the contact areas between the cells, and the sealing due to a high temperature (1000 °C). Also thermal cycling is a problem. This limits the application of these systems. Research on medium-temperature solid oxide fuel cells has been performed, in which the cells are hydrogen-oxygen cells, the solid material is hydrogen-exchanged β -alumina. The operating temperature for this type of solid proton conductor is 150-200 °C.

Internal fuel reforming is also possible. Sulphur is a big problem for all current fuel cell technologies, demanding an expensive gas treatment system, and also significantly decreasing the fuel cell system efficiency. Sulphate based electrolytes are chemically resistant to H_2S and any sulphur containing gases, such as natural gas. The use of Li_2SO_4 as an electrolyte has been tested. This is described in D. Peterson and J. Winnick, J. Electrochem. Soc., 143 (1996) L55.

Catalysts have also been used to increase the output current of conventional fuel cells, which are batteries using galvanic cells powered by hydrogen and oxygen. Generally, such cells are fuelled by hydrogen gas derived from natural gas. There are also other techniques based on methanol, but they have not been successful.

Yet a new type of fuel cell was discovered in 1991, using a catalyst which gave a complete combustion of sugar, thereby forming carbon dioxide and water at a low temperature of just under 100 °C (Larsson Ragnar and Folkesson Börje, Lund University, Sweden.), the so-called "SuFuCell". This cell uses a bio fuel and saves global reserves of petroleum and natural gas. The carbon dioxide produced formed

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in the cell is re-utilised in the photosynthesis to produce new sugar or starch. All kinds of carbon hydrates, such as starch, cellulose etc can be employed.

Although the prior art fuel cells using sugar offer many of above possibilities there is still a demand for a cell with better performance, which is also less expensive.

Summary of the disclosure

An object of the present invention, so called intermediate temperature ceramic fuel cells (ITCFCs), is to provide a fuel cell comprising a ceramic composite electrolyte, which fuel cell does not suffer from the drawbacks described above.

This is embodied in a ceramic membrane (CM) (electrolyte) and a ITCFC provided with such a membrane, according to the invention, which membrane (electrolyte) is based on salt-oxide ceramic composites.

According to a preferred embodiment of the invention, the ceramic membrane (electrolyte) is dense and gas tight.

According to another preferred embodiment of the invention the membrane (electrolyte) is oxygen ion conducting, for instance based on ceria based oxide composites, such as gadolinium doped ceria (CGO) and salt and possibly other inorganic compounds, to operate in ITSOFCs (300 to 800 °C) (Intermediate Temperature SOFCs).

According to another preferred embodiment of the invention, the membrane (electrolyte) is proton conducting ceramic composites based on halide- and hydrohalide-based ceramics, to operate in ITCFCs (Intermediate Temperature CFCs). Composite is referred to as a mixture with at least two different separated phases.

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According to another preferred embodiment of the invention, there is provided a fuel cell, comprising

a fuel chamber

5 an anode,

a cathode,

an electrolyte disposed between the anode and cathode,

an oxidant chamber, wherein said chambers and enclose said anode, cathode and electrolyte,

10 wherein a fuel flowing from the fuel chamber, such as hydrogen is oxidised at the anode, thereby producing electrical energy, wherein said electrolyte is a ceramic composite electrolyte comprises at least one salt and at least one oxide.

15 In some extreme cases, the electrolyte can also have no oxide phase, being a two phase salt/inorganic compound, comprising at least one solid state phase, such as two fluoride phases, or one fluoride with one molten phase, MOH (M = Li, Na, K) etc.

Preferably, the electrodes, i. e. the anode and cathode, are porous.

20 The electrolyte can comprise up to 99 % salt and the salt can be in solid or molten state. Also in some cases, 100% salts with two phases, e.g., two fluorides (chlorides) or fluorides mixed with other pure salts, e.g., MH_x (M = Li, Na, Ca etc., $x = 1, 2$) or $MClx$ (M = Li, Na, Ba, Sr etc., $x = 1, 2$) are possible.

25 The salt (molten or solid state)-oxide composites (SOC) can be selected from all salts and oxides that can make the SOC material function as a specific conductor for particular ions such as H^+ , O^{2-} , or of other ionic charge, e.g., cationic Li^+ , Na^+ , K^+ , or anionic, CO_3^{2-} , Cl^- and F^- etc.), or a mixture thereof. Specific suitable salts and
30 oxides can be such as various natural salts, NaCl etc., and oxides such as Al_2O_3 etc., and synthesised compounds having similar properties.

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Specific examples of SOC's comprise for instance: i) chlorite salts and composites which can have good Cl⁻ conduction. Therefore, the fuel cell according to the invention can also be used for treating industrial waste chlorine gas. ii) fluoride/hydrofluoride-based alumina composites can have excellent proton conduction.

5 iii) Also in some cases, pure salt systems, e.g., two fluorides (chlorides) or fluorides mixed with other pure salts, e.g., MH_x (M = Li, Na, Ca etc., x = 1, 2) or MCl_x (M = Li, Na, Ba, Sr etc., x = 1, 2) for proton conduction.

10 In some extreme cases, the electrolyte can comprise salt, say, two fluoride phases to 100%.

15 The oxide can be almost any suitable oxide, such as alumina, causing significant electronic and ion conduction. It is important that the material in the electrolyte is highly ion conducting.

20 The fuel employed can for instance be H₂ or twon gas.

25 The intermediate temperature (300 - 800°C) allows use of cheap metals as electrode and interconnecting materials, which avoids high temperature (1000 °C) material and technical problems and also reduces the cost.

30 Furthermore, the fuel cell according to the invention can operate as a ceramic membrane electrochemical reactor. Fabrication techniques developed for inorganic membranes such as extrusion, tape casting and doctor-blade for porous ceramic support, tape casting, sol-gel/suspension, CVD techniques for both porous electrodes and dense electrolyte membranes, can also be readily employed in the fabrication.

For constructing high voltage devices, all current high performance oxide electrodes such as various binary oxides, A_xByO_z (A, B = Li, Mg, Ca, Sr, Cr, Fe, Co, Ni, Cu,

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Y, La, Ce, Zr, Ti, etc.), e.g., $Ce_{1-x}BxO_{2-y}$, MnO_2 and $La_{1-x}SrxMnO_3$, and salt-oxide ceramic composite electrodes can be employed.

Since the device, in some cases, has the character of a combination of different galvanic cells, e.g., fuel cells and battery, a higher voltage than that of fuel cells can be achieved.

The device according to the present invention is as an ideal source for high power generation. One reason is because the materials comprised in the device are available in large amounts and highly cost effective. In addition, there is no need for expensive catalysts as in conventional low temperature fuel cells, i. e., operating below $200\text{ }^{\circ}\text{C}$. The device according to the invention can function at intermediate temperatures, say, 300 to $800\text{ }^{\circ}\text{C}$.

The results obtained from the fluoride-based ceramic composite electrolyte fuel cells show a short circuit current density close to 1000 mA/cm^2 and peak power of 180 mW/cm^2 , which is below 300 mA/cm^2 (0.6 V), at $750\text{ }^{\circ}\text{C}$, see Fig. 1. However, there is a large potential for further development, since the results are obtained for bulk and raw disk-type electrolytes only. It can be expected that performance will be significantly improved by a person skilled in the art, by using this technology. The key issue is to optimise electrolyte by employing ceramic membrane technologies, and develop more efficient and compatible electrodes for the new CFCs, which are also claimed.

Brief description of the drawings

The present invention will now be described in more detail with reference to preferred embodiments of the invention, given only by way of example, and illustrated in the accompanying drawings, in which:

Fig. 1 illustrates a fuel cell according to the invention;

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Fig. 2 illustrates time dependence of an open circuit voltage (OCV) at 450 °C according to one embodiment of the invention;

Fig. 3 illustrates temperature dependence of the OCV according to one embodiment of the invention;

Fig. 4 illustrates a typical current-voltage (I-V) characteristic of a fuel cell device using commercial NaCl salt as one of the main components of the electrolyte.

Fig. 5 illustrates a typical I-V characteristic of a fuel cell device using the hydro-fluoride-based composite electrolyte.

Fig. 6 illustrates discharge curves for the fuel cell illustrated in Fig. 5 during operation with various current outputs.

Detailed description of the preferred embodiments

Referring to Fig. 1, the fuel cell 1 according to invention essentially consists of two porous electrodes 2 separated by a dense, proton (or oxygen) conducting salt-oxide (or composite) electrolyte 3, where anode 2a and cathode electrodes 2b can be made of e.g., spinel or perovskite oxides, and the fuel and oxidant chambers 4 surrounding said electrodes 2 can be made of a metal, such as stainless steel.

The fuel circulates in the fuel chamber and part of the fuel is oxidised at the anode. At the same time air is oxidised at the cathode.

Because of the electrochemical cell reaction: $H_2 + 1/2 O_2 = H_2O$ at the cathode side, the formation of the cell reaction product, H_2O can be exhausted together with the air (oxygen), so that the fuel can be re-cycled without requiring water elimination. Thus, it is easy to simplify the device, reduce the fuel cost and also increase the efficiency of the fuel-energy conversion.

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The free energy change of the combustion of the device in Fig. 1 corresponds to an open cell voltage (OCV) of 1.23 V at ambient temperature (25 °C). For high temperatures, this OCV value follows a linear decreasing curve, between 1.0 to 1.2 V. The device can reach a voltage of up to 1.8 V, which is only achieved for limited electrode pair materials. Such a high cell voltage is assumed to be caused by a combination of battery and fuel cell effects.

Current Output and Operating Efficiency

In Fig. 5. A current output of 300 mA/cm² at a cell voltage 0.6 V at 740 °C, corresponded to a power of 180 mW/cm². The cell voltage operating electricity efficiency is $0.6/1.2 = 50\%$. This efficiency can be further increased by the electrolyte conductivity and compatible electrode materials. Most power loss during operation is recognised due to the interfacial loss, since the oxide electrodes are not excellently compatible with the salt electrolytes.

Voltage

Voltages depended on both electrolytes and electrodes. An example of the unusual high voltage device is constructed as:

Doped NiOx /salt-oxide ceramic composites/LaSrCoFeO.

Materials

Composites of salts, specially, chlorides, fluorides and hydro-type-halides containing MH_x etc., and oxides have been successfully synthesised for electrolyte materials, and some of them used also as electrode materials, for intermediate temperature, say 300 to 800°C, fuel cell (ITFC) devices. The materials can use natural resources and synthesising technique has a great flexibility in selection of materials, and advantages of easy preparation, large scale products available and high cost effective.

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It is possible to use synthesised salt-alumina composite containing min. 99.9% salt, e.g., NaCl as main components to prepare proton conducting salt-oxide composite ceramics. A fuel cell device using MCl_x - based composite electrolyte has achieved 1.0 to 1.4 V cell voltage between 350 to 700°C, and several hundreds of mA/cm² can be drawn from this fuel cell.

Due to an excellent chemical stability of sulphate-based electrolytes with H₂S, the fuel cell can use H₂S as fuel, which may work as a desulphonication device for sulphur recovery and treatment of hazardous gases. The device can be continuously operated with stable current output. During the operation, sulphur and water were collected from the anode and cathode, respectively, indicating success in H₂S removal and electricity generation. Thus, it is possible to use natural gas, coal and other sulphur containing gas as fuels without a high extra cost compared to a traditional clean-up station, due to the extra electricity production.

CFCs using the fluoride based electrolytes have may use various liquid fuels for operation. The direct use of logistic fuels such as ethanol or kerosene will simplify the introduction of the fuel cell technology into the commercial market. It is possible to use ethanol or even gasoline as fuel.

The ITCFCs show unique advantages for operating liquid fuels due to high proton conduction and fast electrode kinetics in the intermediate temperature region, without use of noble catalysts. A direct ethanol CFC device has been operated up to 200 mAcm⁻² at 700 °C.

Some more examples are merely intended to illustrate the invention, and are not limiting.

Examples

Unusual examples

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Example 1

In ambient atmosphere, the device according to the invention, illustrated in Fig. 1 showed an OCV between 0.4 to 0.6 V, for both electrodes, whereby the current that could be drawn out rapidly decreased. As long as hydrogen was supplied to the anode of doped NiOx, and air to the cathode of LaSrCoFeO, the OCV suddenly jumped to about 1.0 V, and increased with time gradually to about 1.5 to 1.8 V. When the hydrogen supply was removed, the OCV first dropped steeply then decreased gradually with time. These observations are schematically shown in Fig. 2. Further tests were done by exchanging the electrode sides, i.e., the hydrogen was supplied to the LaSrCoFeO electrode, and air to the doped NiOx electrode, whereby the device showed an OCV close to the former OCV value but with negative sign.

Fig. 3 shows two curves for devices according to the invention using different salt electrolytes. Several tens to hundred of mA/cm² can be taken out from the devices. A typical current density-voltage curve (I-V curve) is shown in Fig. 4.

Example 2 (non electrode construction)

When using only electrolyte GdxCe1-x pellet to achieve fuel cell devices without electrodes, an OCV of such a "non-electrode construction" fuel cell device is 0.96 V, i. e., about 0.2 V higher than conventional constructions with electrode using the same electrolyte. Only about 2 mA/cm² can be taken out from this device. The function is based on the fact of the ionic conducting bulk material, GdxCe1-x as the electrolyte, on each of its surface, whereby the significant electronic and ionic conduction can be caused when reacting with the gas and function as anode and cathode, respectively. It is discovered that the performance of this device was recognised to be limited by the air surface, because in the air (or oxygen) the GdxCe1-x does not create enough electronic conduction, resulting in that an improved construction was made using only one electrode, of e.g., Pt or Ag (paste) for the cathode, i.e.,

(H₂)GdxCe1-x /Pt or Ag (air)

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In this device, the current can be increased by almost one order of magnitude. The further improvement can be done regarding the ion-doping technique to prepare sufficient electronic conducting ceria-based materials. It can be seen clearly from this fuel cell device without using electrode materials, that the SOFC technology will be greatly simplified and more cost effective. Using doped Bi_2O_3 -based oxides instead of doped ceria-based oxide electrolytes will improve cell performance to a large extent.

Example 3 (practical devices)

Fuel cells using the fluoride and hydrofluoride-based composite electrolytes (proton conducting type) and ceria-salt (halides) composite electrolytes are typical examples for practical ITCFC devices, one example is shown in Fig. 5. All these new type ITCFCs have demonstrated a performance well reach the present commercialising standards. In addition, ITCFCs using the sulphate-based electrolytes as the high sulphur tolerant device can treat high sulphur containing fuels, e.g., natural gas or by-products from the refining petroleum process, and at the same time to produce the electricity. This sulphur tolerant CFC device can be expected as the gas-pre-treatment station combined with MCFC power plant to invent a new power generation technology.

It will be appreciated by those skilled in the art that the examples mentioned above are primarily for the purpose of illustration and are not meant to imply any limitation of the present invention.

Claims

1. A fuel cell for production of electrical energy, comprising
a fuel chamber (1)
5 an anode (2a),
a cathode (2b),
an electrolyte (3) disposed between said anode and said cathode,
an oxidant chamber (4), wherein said chambers (1) and (4) enclose said anode, cathode
and electrolyte,
10 characterised in that:
said electrolyte (3) is a ceramic CSC (ceria salt composite) electrolyte comprising at
least one salt and at least one ceria phase.
2. A fuel cell according to claim 1, wherein the electrolyte comprises salts selected
15 from salts that can make the CSC material function as a specific conductor for
particular ions such as H^+ , O^{2-} , or of other ionic charge, e.g., cationic Li^+ , Na^+ , K^+ , or
anionic, CO_3^{2-} , Cl^- and F^- etc., or a mixture thereof, preferably natural salts, e.g. NaCl.
3. A fuel cell according to claim 1 or 2, wherein the electrodes comprises binary
20 oxides, such as $A_xB_yO_z$ (A, B = Li, Mg, Ca, Sr, Cr, Fe, Co, Ni, Mn, Cu, Y, La, Ce, Zr,
Ti, etc.), typically, Li_xMO_y (M = Ni, Co, Mn), $Ce_{1-x}B_xO_{2-y}$, MnO_2 and
 $La_{1-x}Sr_xMn(Co)O_3$.
4. A fuel cell according to claim 1, wherein the electrolyte is sulphate-based CSC for
25 sulphur containing fuels, intended to operate as a high sulphur tolerant CFC device,
acting as a pre-gas treatment station and intended to be combined with MCFC power
plants.

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PCT International Application

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10 October 2000

Claims

1. A fuel cell for production of electrical energy, comprising
a fuel chamber (1)
5 an anode (2a),
a cathode (2b),
an electrolyte (3) disposed between said anode and said cathode,
an oxidant chamber (4), wherein said chambers (1) and (4) enclose said anode, cathode
and electrolyte,
10 characterised in that:
said electrolyte (3) is a ceramic CSC (ceria salt composite) electrolyte comprising at
least one salt and at least one ceria phase.
2. A fuel cell according to claim 1, wherein the electrolyte comprises salts selected
15 from salts that can make the CSC material function as a specific conductor for
particular ions such as H^+ , O^{2-} , or of other ionic charge, e.g., cationic Li^+ , Na^+ , K^+ , or
anionic, CO_3^{2-} , Cl^- and F^- etc., or a mixture thereof, preferably natural salts, e.g. NaCl.
3. A fuel cell according to claim 1 or 2, wherein the electrodes comprises binary
20 oxides, such as $A_xB_yO_z$ ($A, B = Li, Mg, Ca, Sr, Cr, Fe, Co, Ni, Mn, Cu, Y, La, Ce, Zr,$
 Ti , etc.), typically, Li_xMO_y ($M = Ni, Co, Mn$), $Ce_{1-x}B_xO_{2-y}$, MnO_2 and
 $La_{1-x}Sr_xMn(Co)O_3$.
4. A fuel cell according to claim 1, wherein the electrolyte is sulphate-based CSC for
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plants.

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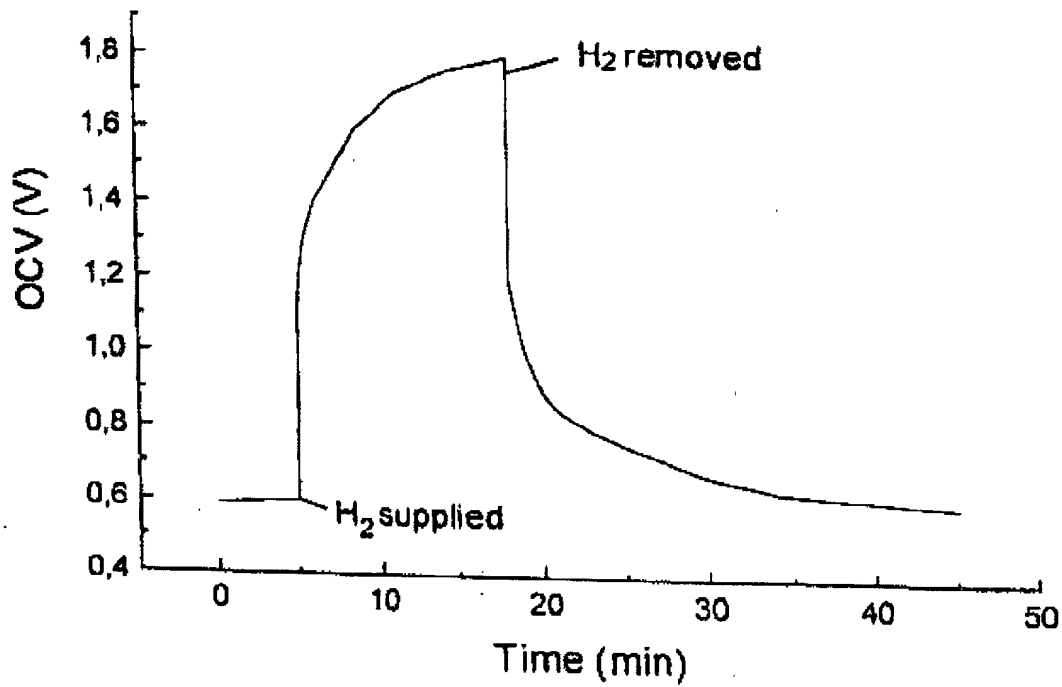


FIG. 2

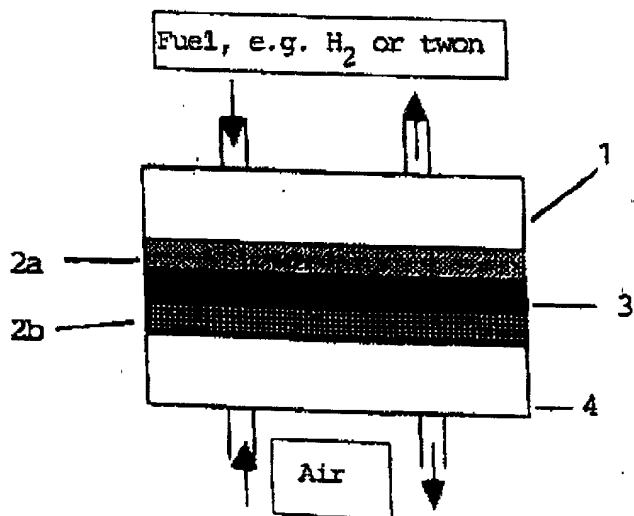


FIG. 1

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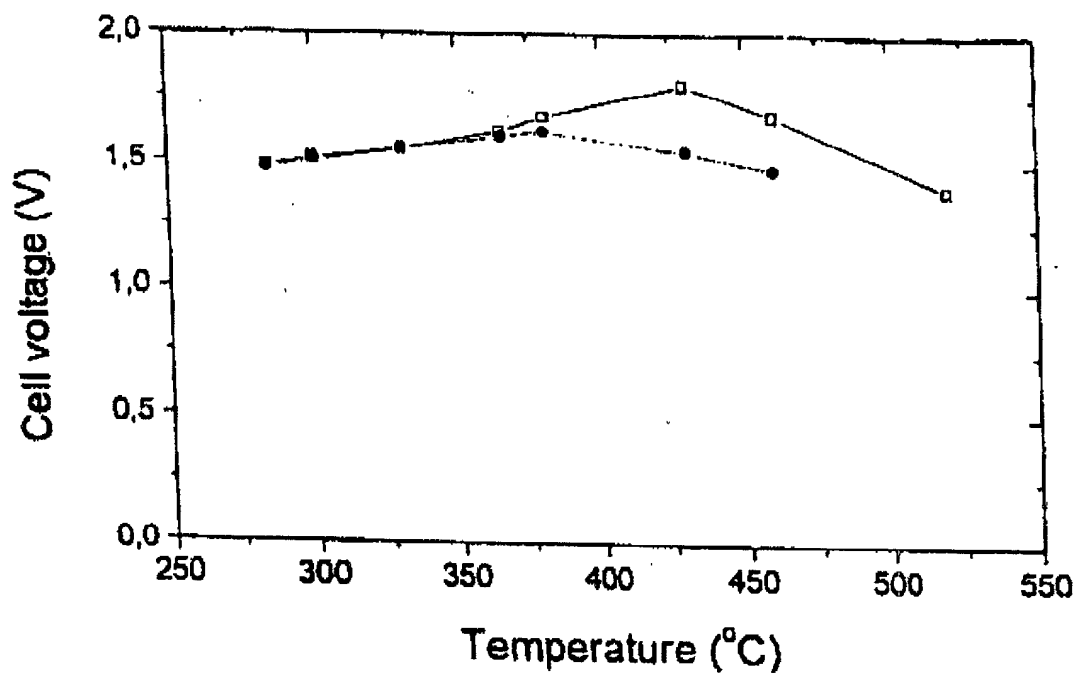


FIG. 3

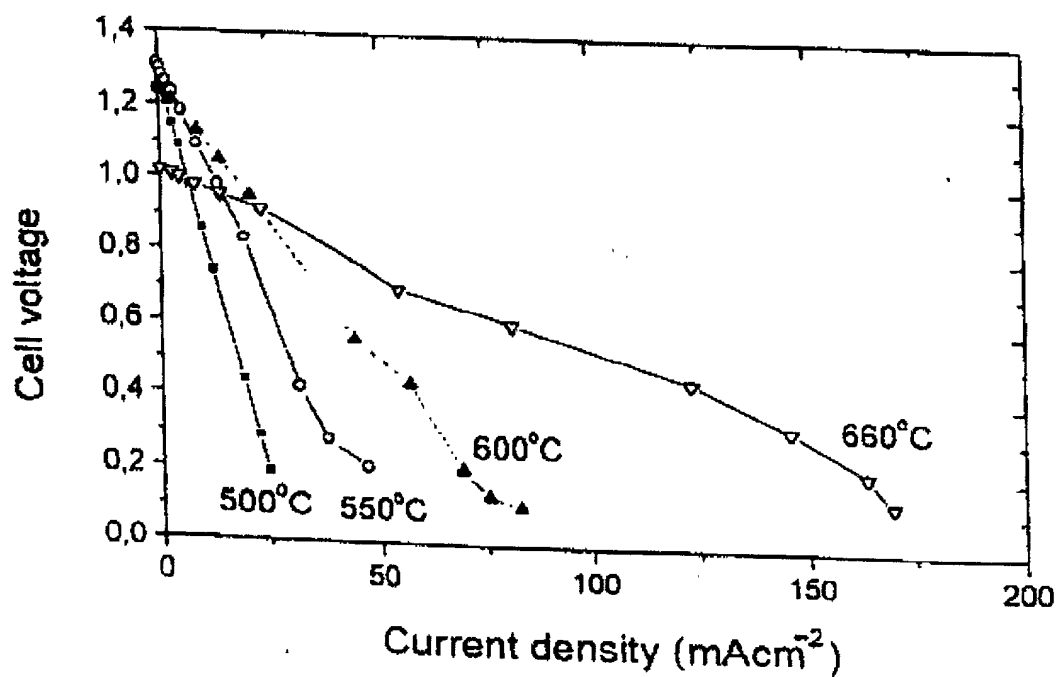


FIG. 4

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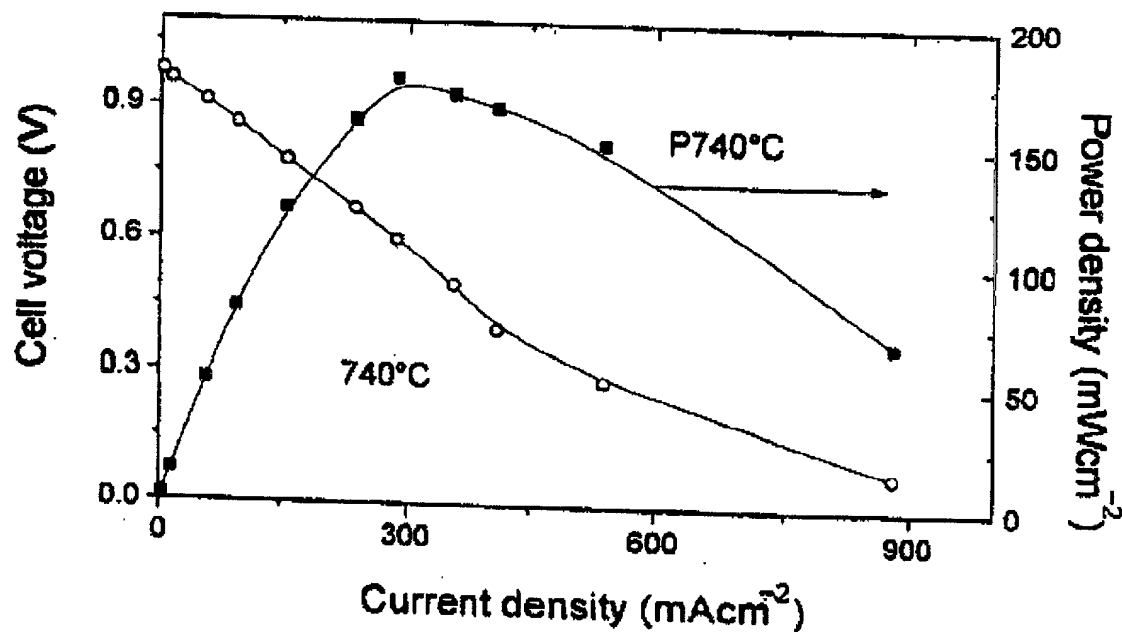


FIG. 5

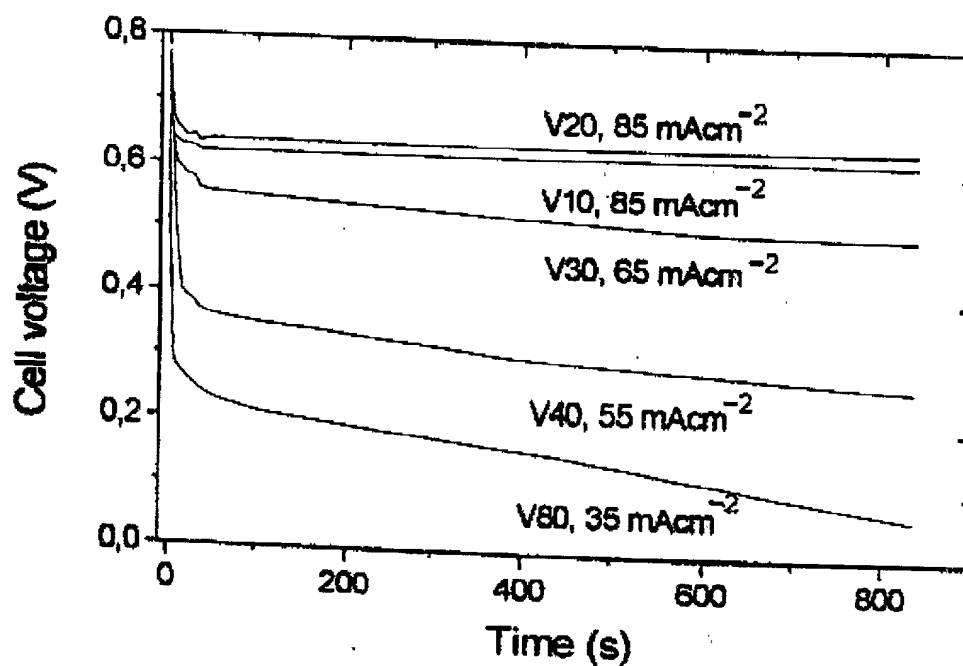


FIG. 6

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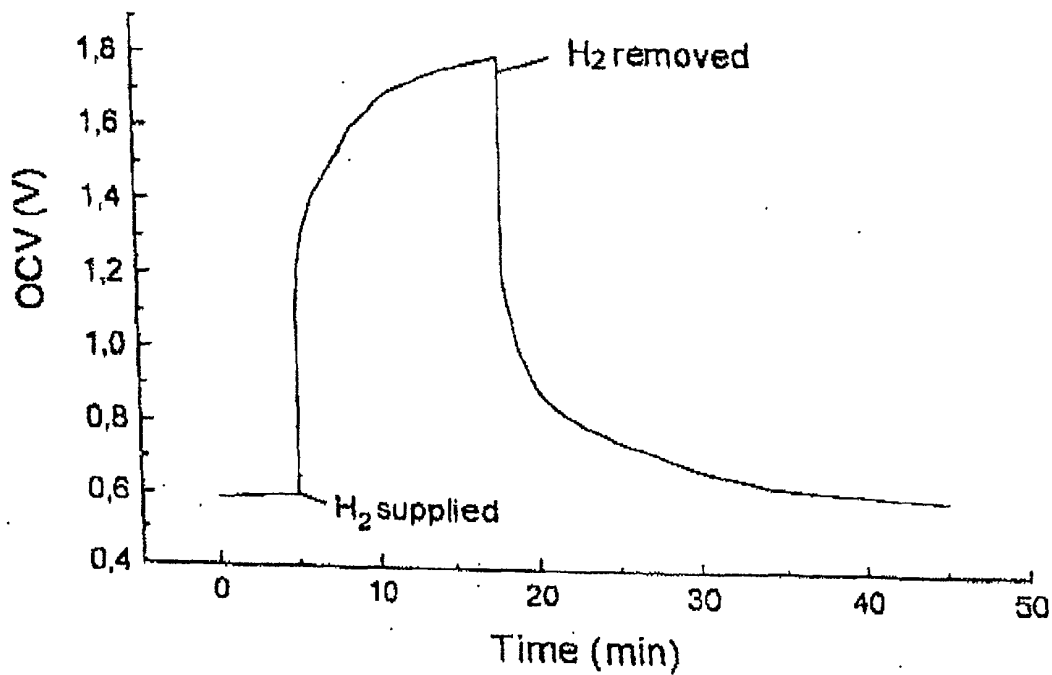


FIG. 2

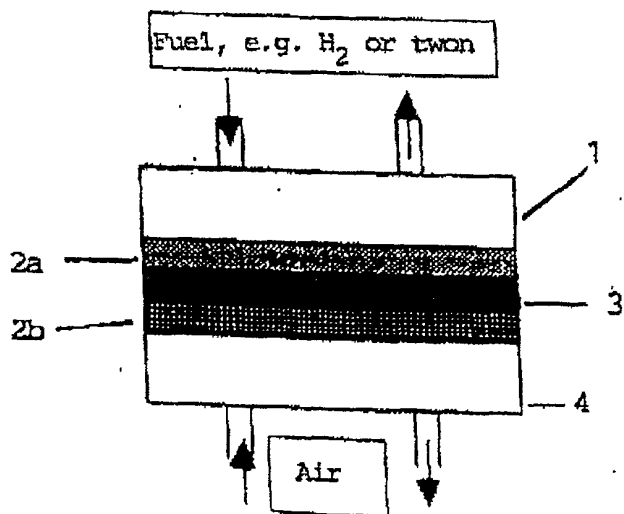


FIG. 1

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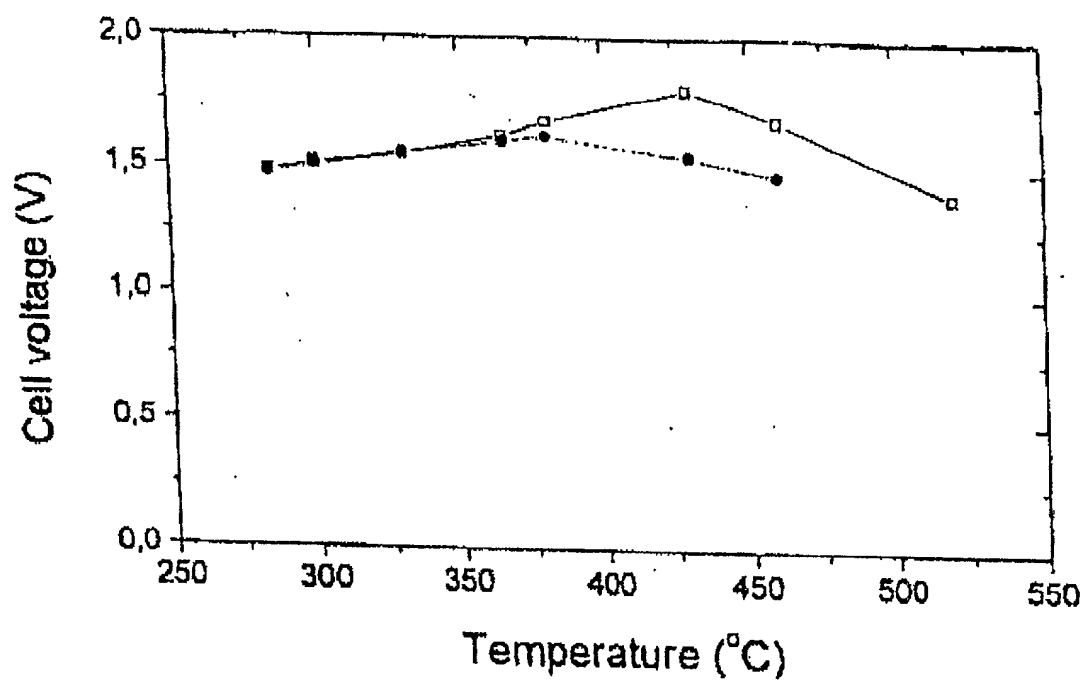


FIG. 3

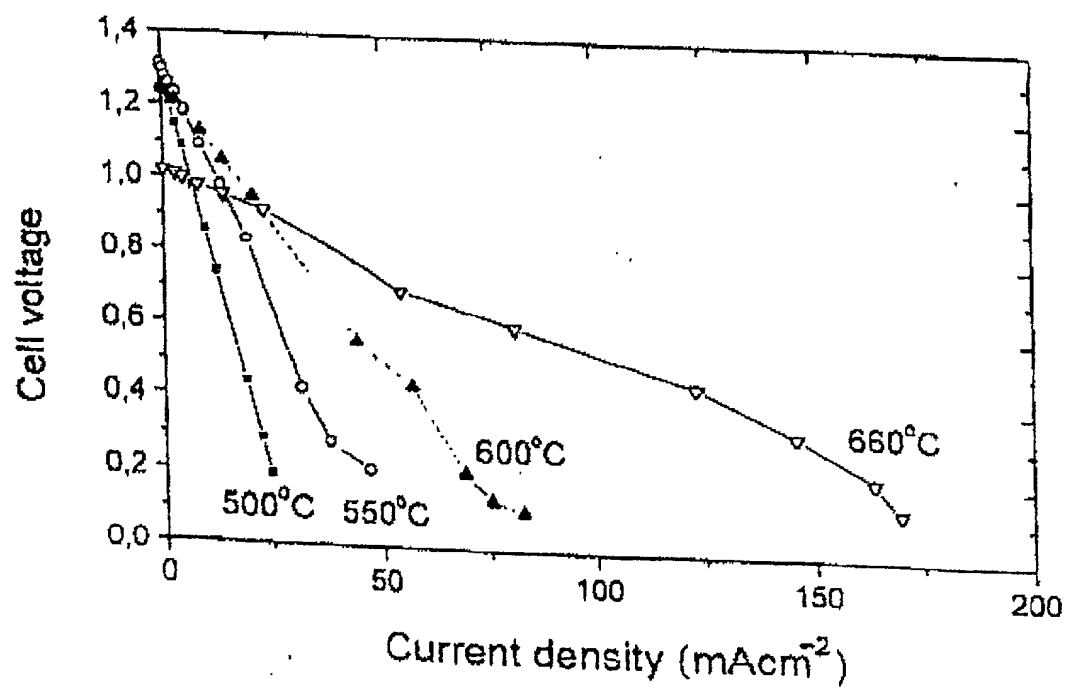


FIG. 4

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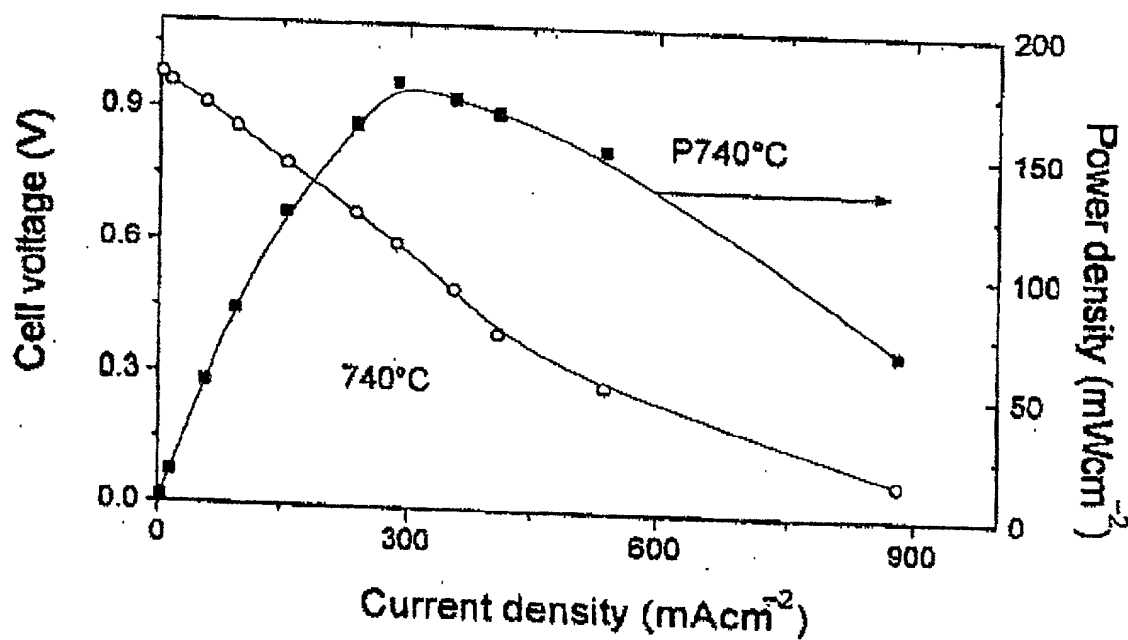


FIG. 5

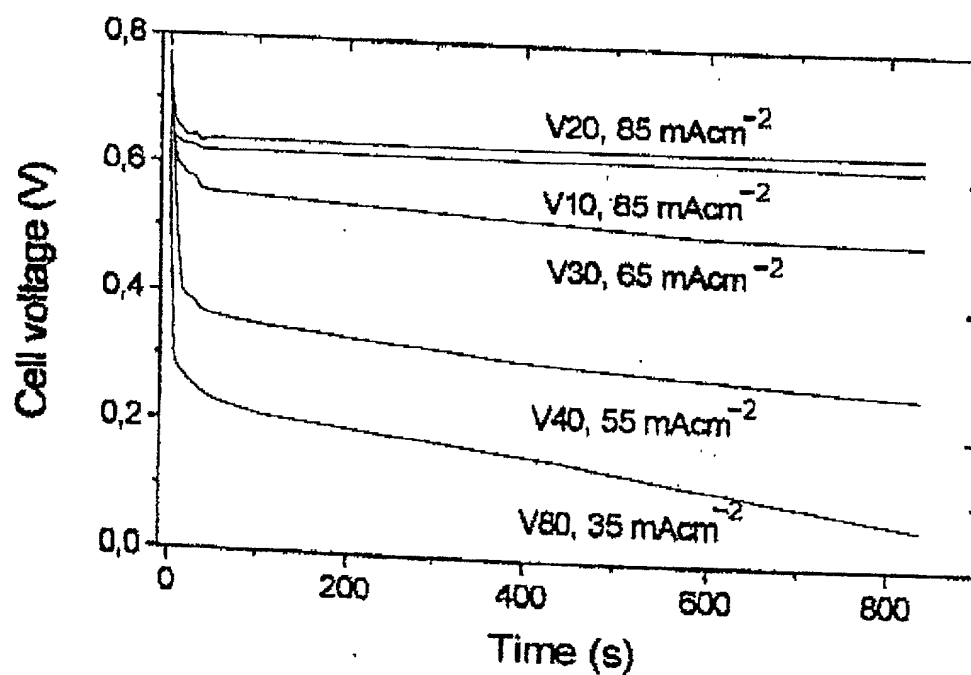


FIG. 6

SUBSTITUTE SHEET (RULE 26)

COMBINED DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

A FUEL CELL

the specification of which: *(check one)*

REGULAR OR DESIGN APPLICATION

☒ is attached hereto.

☐ was filed on _____ as application Serial No. _____ and was amended on _____ (if applicable).

PCT FILED APPLICATION ENTERING NATIONAL STAGE

☐ was described and claimed in International application No. _____ filed on _____ and as amended on _____ (if any).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

PRIORITY CLAIM

I hereby claim foreign priority benefits under 35 USC 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

PRIOR FOREIGN APPLICATION(S)

| Country | Application Number | Date of Filing (day, month, year) | Priority Claimed |
|---------|--------------------|--------------------------------------|------------------|
| Sweden | 9802103-3 | 12 June 1998 | yes |
| | | | |

(Complete this part only if this is a continuing application.)

I hereby claim the benefit under 35 USC 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of 35 USC 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

PCT/SE99/01046
(Application Serial No.)

11 June 1999
(Filing Date)

pending
(Status--patented, pending, abandoned)

POWER OF ATTORNEY

The undersigned hereby authorizes the U.S. attorney or agent named herein to accept and follow instructions from Albihns Stockholm AB as to any action to be taken in the Patent and Trademark Office regarding this application without direct communication between the U.S. attorney or agent and the undersigned. In the event of a change in the persons from whom instructions may be taken, the U.S. attorney or agent named herein will be so notified by the undersigned.

⑤ As a named inventor, I hereby appoint the following attorney(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: Robert J. PATCH, Reg. No. 17,355, Andrew J. PATCH, Reg. No. 32,925, Robert F. HARGEST, Reg. No. 25,590, Benoît CASTEL, Reg. No. 35,401, Alan W. YOUNG, Reg. No. 37,970, c/o YOUNG & THOMPSON, Second Floor, 745 South 23rd Street, Arlington, Virginia 22202.

Address all telephone calls to Young & Thompson at 703/521-2297.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

0017036850573
Full name of sole or first inventor: Bin Zhu

(given name, family name)

Inventor's signature [Signature]

Date 6 December 2000

Residence: Stockholm, Sweden

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Citizenship: Chinese

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Full name of second joint inventor, if any: _____

(given name, family name)

Inventor's signature _____

Date _____

Residence: _____

Citizenship: _____

Post Office Address: _____

Full name of third joint inventor, if any: _____

(given name, family name)

Inventor's signature _____

Date _____

Residence: _____

Citizenship: _____

Post Office Address: _____